DRYING OF BULK SILICA GELS MOLDED FROM TETRAETHYLORTHOSILICATE AND AEROSIL

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The physicochemical specifics of the process of drying of bulk silica gel molded from mixed sols (tethraethylsilicate hydrolyzate : aerosil) are considered. The results of the experimental studies of kinetic drying curves of bulk-formed silica gels depending on the process conditions and modes are presented.

A problem arising in production of quartz glass using the sol-gel method consists in the need to preserve continuous gels without their cracking and disintegration into fragments in drying [1].

Methods proposed for successful drying in the sol-gel process include introduction of chemical additives which control the drying process [2, 3], as well as some variants for the synthesis of sufficiently strong large-pore gel from alkoxide-derivative fractal particles and Aerosil (silica powder) in mixed colloid-silica systems [4]. Introduction of aerosil into a sol with its subsequent ultrasonic activation makes it possible to obtain large-sized silica gels of complex shapes with a relatively high percentage of acceptable blanks [5].

The phases of synthesis of high-purity quartz glass using aerosil and the physicochemical parameters of xerogel are discussed in detail in [6], however, the results of the study of the drying process were not published earlier.

The present study considers the processes of drying in silica gels produced in the $Si(OC_2H_5)_4 - C_2H_5OH - H_2O - HCl$ system. The modifying additive to sol in this case was aerosil T-30 (Germany) with specific surface area 300 m^2/g and average particle size 7 nm. Hydrolysis of the mixture was carried out with the following molar ratio of the components: $Si(OC_2H_5)_4 : C_2H_5OH : H_2O : HCl = 1 : 2.5 : 16 : 0.01$ in the conditions of active stirring by a mechanical mixer. After the reaction of hydrolysis of tetraethylorthosilicate (TEOS) was completed, aerosil in the amount of 70 wt. % was added to the hydrolyzate, and the mixture was subjected to ultrasonic activation (frequency 42 kHz, voltage 500 W, duration 2 h). An aqueous solution of ammonia was used as the gel-forming agent. Next, the mixed gel was poured into hydrophobic molds and capped with tightly sealed lids. After

gel formation, the molds were opened and the gels were held in distilled water for 3 days at room temperature with the aim of maturing and removing the solvent, chlorine, and ammonium ions. After that, the gels were extracted from water and dehydrated.

The drying kinetics of the formed silica gels was studied using a VV-02 electronic scale/moisture gage in the temperature range 20 – 150°C with accuracy of weight measurement ± 0.5 g. The samples were placed on the scale pan in the open state and in cardboard boxes (containers).

Experimental studies of drying processes were carried out under static conditions at room temperature and under dynamic conditions, when the samples were circumvented by a laminar air current arising due to convection, as the samples were heated from underneath. Furthermore, the effect of the shape of samples on the processes taking place in drying was investigated. The absolute modifications of the weight and diameter of the disk-shaped samples ($D = 80$ mm, $h = 10$ mm) were determined at different temperatures (20, 60, and 100°C) and relative humidity 45 – 50%.

It was experimentally found that the ethanol : TEOS ratio in the synthesis of xerogel using aerosil T-30 in the four-component system $Si(OC_2H_5)_4 - C_2H_5OH - H_2O - HCl$ also has an effect on the linear shrinkage in gel drying (60°C, 7 days). The highest linear shrinkage is typical of samples obtained with a lower (by 10%) content of solvent. This is most probably related to the increased strength of the silicon-oxygen lattice, more homogeneous structure of the globular frame, and a greater specific volume of the pores.

The drying rate largely depends on temperature (Fig. 1). Three segments can be distinguished on the plots representing variations in the weight of disk-shaped samples versus the duration of the dehydration process (at 20°C): *1*) period of fast weight decrease accompanied by a uniform decrease

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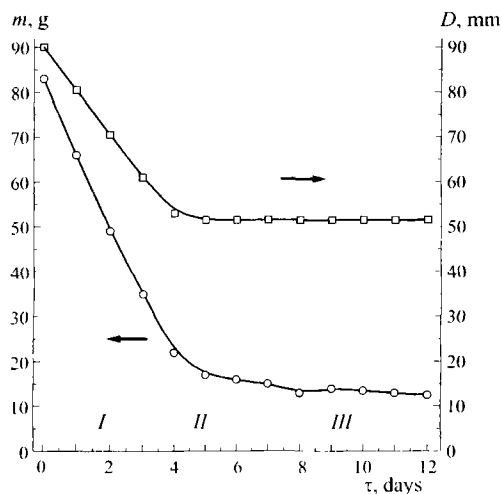
Fig. 1. Drying kinetics of gel samples under stationary conditions (temperature 20 ± 2°C, relative humidity 50%).

Fig. 2. Capillary pressure Δp versus the pore radius r.

Fig. 3. Gel texture model (a) and gel lattice element (b).

in the cross-lateral size of the samples; II) transition zone, and III) period of slow weight decrease. It should be noted that after the end of the first period, the linear dimensions of the sample virtually do not change; i.e., at the initial stage of drying, the rate of evaporation of liquid from the gel is constant and coincides with the rate of variation of its linear dimensions or the rate of compression of the porous structure. The liquid completely fills the gel pores, and the volume shrinkage of the gel is equal to the volume of the evaporated liquid. As the gel shrinks and the maturing processes in it continue, its strength and hardness grow.

During the transitional period, the liquid meniscus starts penetrating into the gel, and transport of the liquid to the surface is carried out by means of flowing over the pore surface. Insignificant shrinkage occurs at this time due to polycondensation processes and hardening of the pore walls.

During the third period, the transport of liquid to the surface and removal of liquid are implemented through evaporation and vapor diffusion over the pore surface. In this period, the linear dimensions of the gel do not change, and the weight loss is insignificant. The most critical is the transition period, when the hardened walls of the silicon-oxygen skeleton have to withstand the capillary pressure forces Δp.

The capillary pressure Δp is proportional to the specific surface energy γ at the liquid-air interface and is in reverse proportion to the pore radius r [7]:

$$\Delta p = \frac{2\gamma\cos\theta}{r},$$

where θ is the contact angle at the liquid – solid – air phase boundaries.

Figure 2 shows the estimated value of Δp as a function of the average pore radius, taking into account the surface energy equal to 0.073 N/m for water and subject to the condition of full wetting of the pore surface ($\cos\theta = 1$). With
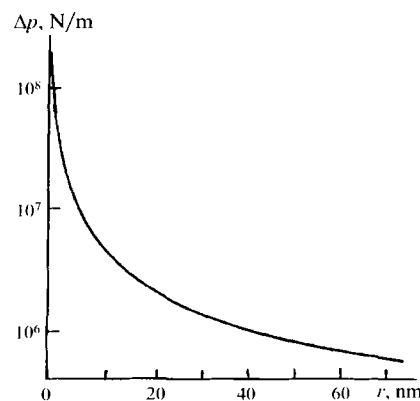
small pore sizes, the capillary forces are substantial, and the pressure of the liquid is transmitted to the pore walls, developing stresses whose maximum is on the pore surface. When the pores are of different sizes, when the walls between them are thin, and when their strength is below the arising stress, cracks arise inside the pores, and during drying, such gel becomes damaged (cracked) and disintegrates into irregular-shaped fragments.

Considering the gel as an agglomerate of randomly arranged spheroid particles with radius R (Fig. 3), the mean coordination number $\langle k \rangle$ can be found from the expression [7]:

$$\langle k \rangle = 2\exp[2.4(1-p)], \tag{1}$$

where p is the share of pores with respect to the solid phase.

There spheres are interconnected by "necks" of the radius α. The force of attraction F between the spheres is written as

$$F = \sigma_{es}, \tag{2}$$

where σ_{es} is the estimated compressive strength of the solid phase (quartz glass).
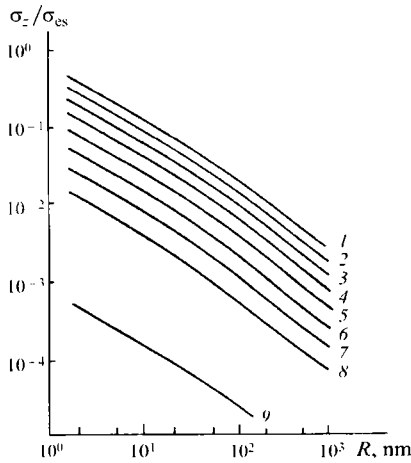
Fig. 4. Estimated curves of mechanical strength of gels depending on particle radius and porosity. Porosity (%): 1) 0.2; 2) 0.3; 3) 0.4; 4) 0.5; 5) 0.6; 6) 0.7; 7) 0.8; 8) 0.9; 9) 0.95.
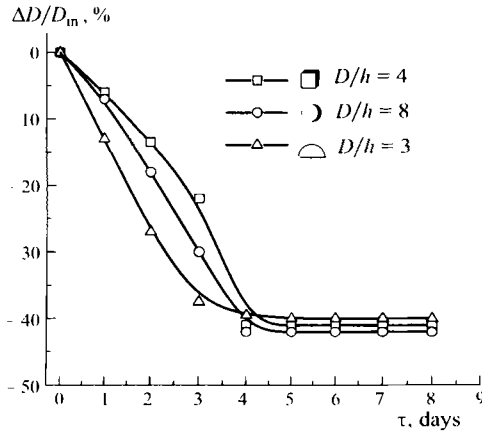

Fig. 5. Relative variation in linear sizes of gels in drying depending on the sample shape (temperature 20 – 22°C, relative humidity 45 – 50%).

For an ensemble of such randomly packed spheres, the strength in the direction z is equal to

$$\sigma_z = 9\langle k\rangle \frac{F(1-p)}{32\pi R^2}.\tag{3}$$

Substituting expressions (1) and (2) into expression (3), we find the ratio σ_z/σ_{es}:

$$\frac{\sigma_z}{\sigma_{es}} = \frac{9}{16}(1-p)\,e^{2.4(1-p)}\left(\frac{\alpha}{R}\right)^2.\tag{4}$$

Thus, it follows from expression (4) that the ratio σ_z/σ_{es} depends on porosity and the ratio α/R. In the final aging of the gel in drying, silica most probably is reprecipitated from the convex sites to the sites with negative curvature radius,
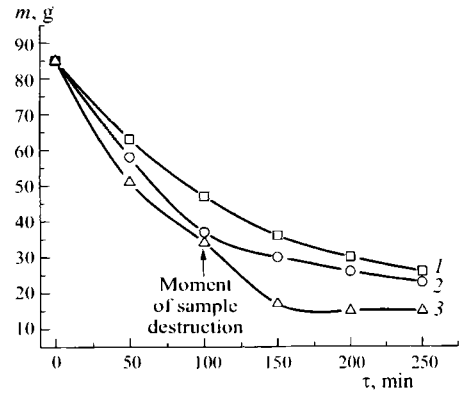

Fig. 6. Kinetics of gel drying in a convective current: 1) 60°C, in a container; 2) 100°C, in a container; 3) 100°C, without container.

which results in the growth of necks between the particles and strengthening of the gel structure. This is facilitated by the presence of easily soluble hydrated silica particles formed as the consequence of hydrolysis and polyconden-sation.

The effective (negative) radius of the necks satisfies the following condition.

$$\frac{2}{r_n} = \frac{1}{\alpha} - \frac{1}{\rho},$$

where ρ is the minimum (negative) curvature radius.

If the particle radius is equal to R, then

$$(R+\rho)^2 = (\rho+\alpha)^2 + R^2.$$

The ratio α/R was calculated for gels consisting of parti-cles of the same size as the radius R, which varies from 2 to 1000 nm. Figure 4 shows estimated curves for the correlation σ_z/σ_{es} with the particle radius and porosity. It can be seen that gels formed from large particles exhibit lower mechani-cal strength due to weaker formation of necks. However, in mixed colloid-silica systems, the strength increases due to decreased porosity and cementing capacity of silicon dioxide fractal particles. Thus, as distinct from uniformly porous gels with pore sizes within the range of 2 – 3 nm [8], mesoporous gels can dry relatively easily without cracking and disinte-gration into fragments.

Complete removal of free water from the gel at tempera-ture 20 – 25°C lasts several days and to a great extent de-pends on the shape and size of the gel, as well as on the tem-perature and moisture of the ambient medium.

Figure 5 shows the relative changes in the linear dimen-sions of gel while dried under stationary conditions, depend-ing on the sample shape (the drying conditions being equal). It can be seen that the sample size has little effect on drying kinetics; however, as the surface area of samples increases (from a parallelepiped to a disk and then to a spheroid sam-
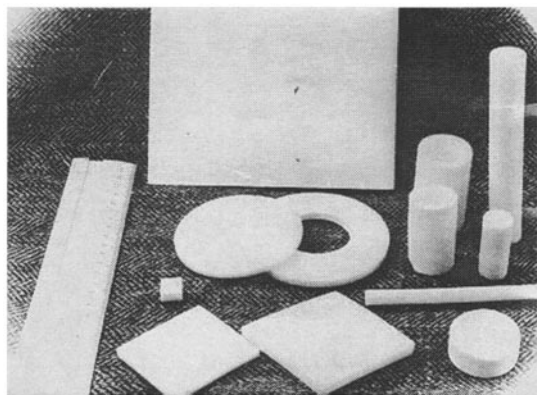
Fig. 7. Dried molded silica gels.

ple), the drying duration substantially decreases, and the shrinkage curve slope at the initial stage of drying is modified.

An increase in the drying temperature modifies the kinetic curves of weight loss, and the curve shape primarily depends on whether the sample is in the free state, or is placed inside a porous container. Fast removal of moisture from the gel (60 and 100°C) results in the destruction of the samples, and this destruction occurs in different variants of the samples within an approximately equal time period: 0.5 – 1 h (Fig. 6).

As the result of a series of experiments, it was found that the optimum range for the rate of moisture weight loss at the first stage of drying, at which rate the sample is not destroyed, is equal to 2 – 5 g/h. This rate can be achieved by using a porous container or a container with a controlled evaporation surface, and the optimum drying temperature for small-sized gels is $60 \pm 5°C$. Large-sized cylindrical or tube-shaped gels can be conveniently dried in a thermostat (the

temperature $30 \pm 1°C$, relative humidity 50 – 60%) in the free state (without containers) on special mounts in a tilted position; otherwise they crack in the second stage of drying.

Using the developed operating modes, drying conditions, and special equipment, gels of various shapes and dimensions were obtained, which serve as intermediate blanks for gel glasses and nanocomposites (Fig. 7). Moreover, they can serve as catalyst substrates, adsorbents, and ultraporous filters and matrices for chemical sensors and biosensors.

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